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Alumina from reprocessing of spent hydroprocessing catalyst

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ABSTRACT

Spent hydroprocessing catalysts that are discarded as solid wastes from the petroleum refining industries contain high concentrations of valuable metals (e.g. Mo, V, Ni, Co) and Al_2O_3. Increasing emphasis has been placed in recent years on developing processes for their recycling and utilization. In the present work, experiments were designed and conducted to extract >99% of all valuable metals as well as to recover the alumina present in the spent catalyst in the form of high purity boehmite. Caustic digestion and hydrothermal treatment methods were used to recover alumina in the form of boehmite as well as to modify its textural properties. γ-Al_2O_3 was prepared from the boehmite by heating at 500 °C. Factors controlling the textural properties of boehmite and γ-Al_2O_3 derived from the recovered boehmite were also investigated as part of the study. The treated samples were characterized by X-ray diffraction, surface area, pore volume, and pore size distribution measurements. Both boehmite and γ-Al_2O_3 with desirable textural properties (i.e. surface area >200 m^2/g; pore volume >0.7 ml/g; mean pore diameter 100–120 Å) suitable for use as catalyst support were obtained by optimizing boehmite hydrothermal treatment conditions.

1. Introduction

In the petroleum refining industry clean fuels are produced by hydrotreating and hydroconversion of petroleum distillates and residues in the presence of solid catalysts [1,2]. Hydrotreating catalysts normally consist of molybdenum supported on an alumina (Al_2O_3) carrier with promoters such as Co or Ni, and they enhance the removal of undesirable contaminants such as S, N and metals (V and Ni) present in the liquid petroleum fractions [3–5]. The catalysts used in the process deactivate with time [6,7] and when the activity declines below the acceptable level, the spent catalysts are discarded as solid wastes. Spent hydroprocessing catalysts contain metals such as Mo, Co, Ni, V and Al_2O_3 together with coke and some residual oil. As these spent catalysts are hazardous wastes [8–10], their disposal in landfills is restricted. Safe handling and disposal of the environmentally hazardous spent hydroprocessing catalysts is a problem of great concern in the petroleum refining industry, and increasing emphasis has been placed on developing process for their recycling and reutilization. Several alternative methods such as regeneration/rejuvenation, metals recovery and preparation of useful materials and active new catalysts, and treatment for safe disposal have been investigated by researchers worldwide to deal with the spent catalyst problem [10–12]. Among these, metals recovery is an attractive option.

The metals (Mo, V, Co and Ni) present in spent hydroprocessing catalysts are highly valuable and have many uses, particularly in the steel industry for making stainless steel and special alloys. Recovery of these metals from the spent catalysts has been studied extensively, and several methods such as acid leaching, alkali leaching, two stage leaching with acid and alkaline solutions, roasting with sodium salts, treatment with ammonia and ammonium salt solutions, chlorination, bioleaching, and electrochemical dissolution have been reported in the literature for recovery of metals from spent hydroprocessing catalysts [13,14].

In some studies, alumina present in the spent catalyst has been reclaimed as aluminium salts [15–17] or as fused alumina [18,19] after recovering the valuable metals such as Mo, V, Ni and Co. Preparation of α-alumina from an alumina-containing spent hydrotreating catalyst was reported in a recent study by Chen et al. [20]. Surprisingly, little effort has been made in the earlier studies to recover the alumina in the form of boehmite [AlO(OH)]. Boehmite is a valuable material and it has a wide range of applications including catalyst supports, coatings, polymer additives, sol–gel abrasives and ceramics. As part of a large research program on recycling and utilization of spent hydroprocessing catalysts, in the present work we have studied the reclamation of the Al_2O_3 present in the spent hydroprocessing catalyst in the form of high purity boehmite after extracting the metals. The factors controlling the textural properties boehmite and γ-Al_2O_3 derived from the recovered boehmite were also investigated as part of the study and the conditions for obtaining high quality boehmite and γ-Al_2O_3 with large surface area and controlled pore size were optimized.

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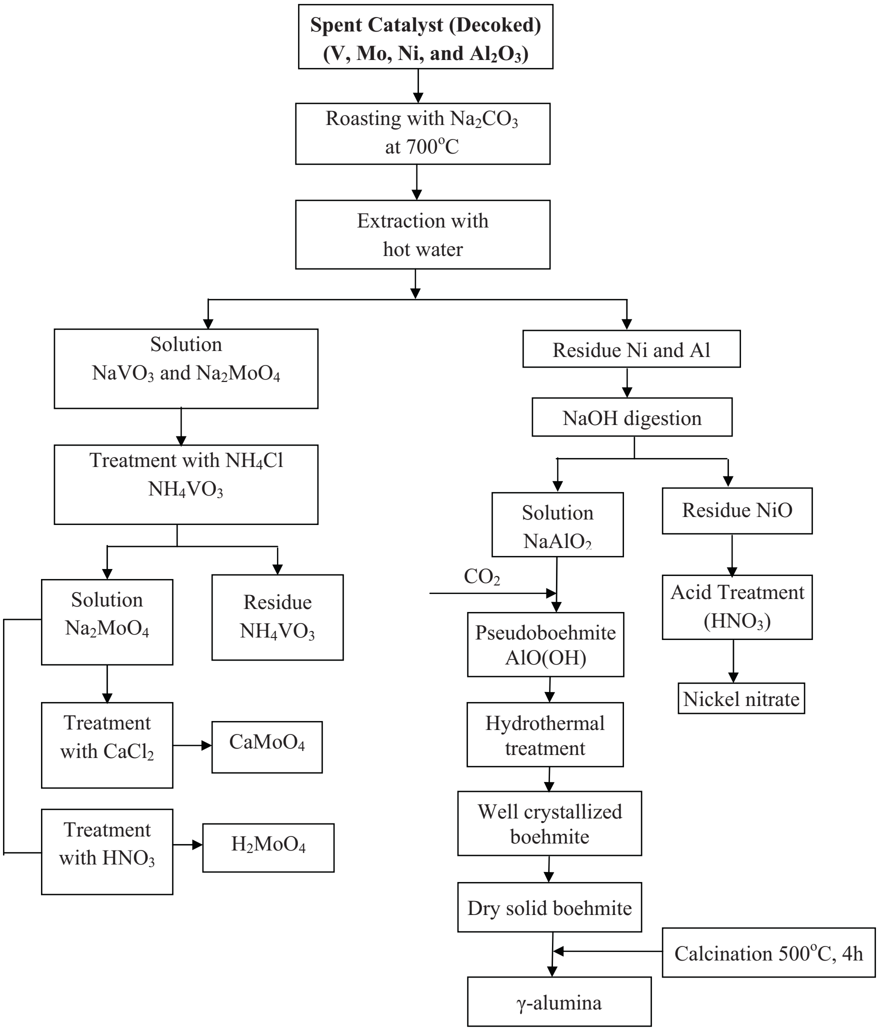


Fig. 1. Simplified flow diagram for recovery of metals and boehmite/γ-alumina from spent hydroprocessing catalyst.

2. Experimental

Spent hydroprocessing catalyst was obtained from Kuwait National Petroleum Company's refinery. It was deoiled, decoked, crushed and ground to fine powder (particle size <500 μm) using standard procedures [21]. The decoked catalyst contained 5.85 wt% Mo, 9.8 wt% V and 4.67 wt% Ni and the balance Al_2O_3. A series of steps such as soda ash roasting, chemical treatment and precipitation, caustic digestion and hydrothermal treatment were used in the present study to recover alumina in the form of boehmite together with reclamation of all valuable metals (Mo, V and Ni) from the spent catalyst. The procedure used is schematically shown in Fig. 1. The surface areas of recovered alumina samples were determined by the BET method using a TriStar 3000 adsorption unit manufactured by the Micrometrics Corporation (New York, USA). Pore volume and pore size distribution of boehmite and γ-alumina samples were determined by nitrogen adsorption using the same equipment. For the surface area and porosity measurement of boehmite, the sample was degassed at 110 °C for 2 h. Degassing at higher temperatures was avoided to prevent dehydration of boehmite and its conversion to gamma alumina. ICP spectrometer (Teledyne-Leeman Labs–Prodigy – High Dispersion ICP) was used to determine the concentration of different metals (Mo, V, Ni, and Al) in the spent catalyst, extracted solutions and in the recovered materials.

3. Results and discussion

3.1. Metals recovery by soda ash roasting process

The metals present in the spent catalyst were first extracted by soda ash roasting process before alumina recovery. Initial studies were focused on determining the optimum conditions for extraction of maximum amounts of Mo and V from the spent catalyst by roasting with Na_2CO_3. The decoked spent catalyst was mixed with Na_2CO_3, and the mix was roasted in the presence of air in a muffle furnace at high temperatures (e.g. 700 °C) to convert the Mo and V present in the spent catalyst to sodium molybdate (Na_2MoO_4) and sodium vanadate ($NaVO_3$), respectively.

$$MoO_3 + Na_2CO_3 \rightarrow Na_2MoO_4 + CO_2\uparrow$$

$$V_2O_5 + Na_2CO_3 \rightarrow 2NaVO_3 + CO_2\uparrow$$

Ni and Al present in the catalyst did not react with Na_2CO_3 under these conditions. A series of experiments were conducted to investigate the effects of roasting temperature, roasting time, and the amount of Na_2CO_3 mixed with the spent catalyst, on the extraction percentage of Mo and V. The results of these experiments are presented in Fig. 2a–c. These results clearly show that the optimum conditions for the maximum recovery (99.7%) of Mo and V in the soda ash roasting process are: temperature = 700 °C; time = 1 h;

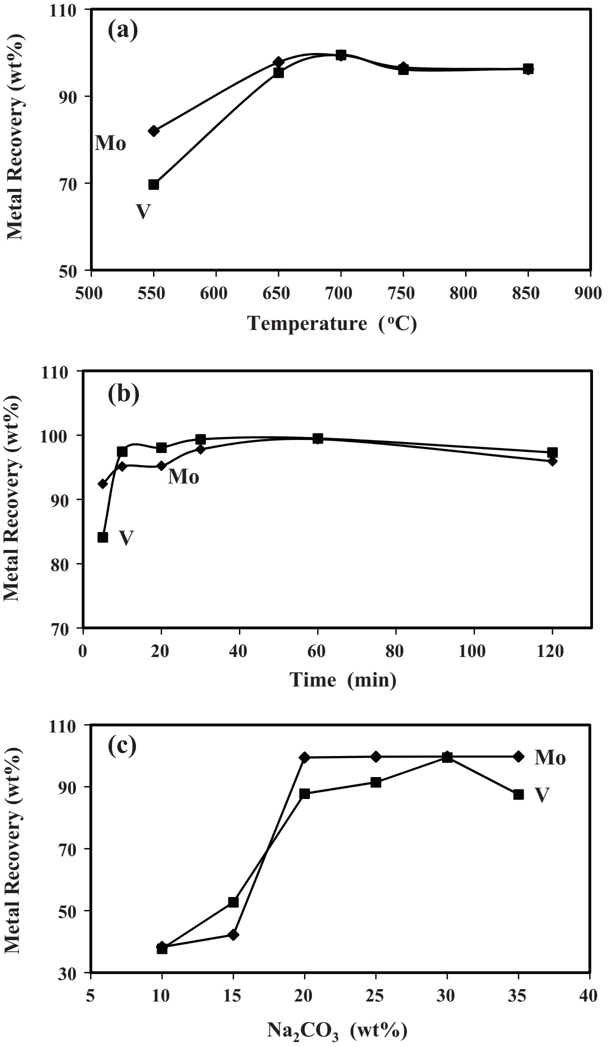


Fig. 2. Effect of process conditions on the extraction of Mo and V from spent catalyst by roasting with Na_2CO_3: (a) temperature, (b) time, and (c) concentration.

Na_2CO_3 amount = 30 wt%. The roasted product was treated with water at 100 °C by continuous stirring to dissolve the Na_2MoO_4 and Na_2VO_3 salts. The insoluble residue containing Ni and Al_2O_3 was separated from the solution containing Na_2MoO_4 and Na_2VO_3 by filtration.

The solution (pH 9.3) containing Na_2MoO_4 and $NaVO_3$ was treated with NH_4Cl solution at 80 °C. Vanadium was precipitated as NH_4VO_3 under these conditions leaving the molybdate in solution.

$$NaVO_3 + NH_4Cl \rightarrow NH_4VO_3 + NaCl$$

NH_4VO_3 was filtered, washed and dried. The recovery of NH_4VO_3 was 96.5%. Its purity was more than 98%. The impurities present in the recovered ammonium vanadate included small amounts of Si (0.1%); Fe (0.08%), Mo (0.08%); Al (0.01%); Na (0.02%) and traces of SO_4, Cl and moisture. XRD patterns of the recovered material (Fig. 3a) showed all characteristic peaks of NH_4VO_3.

The filtrate after removing NH_4VO_3 contained Na_2MoO_4. Two methods were used in the present study for the recovery of Mo from the sodium molybdate (Na_2MoO_4) solution. In the first method, the sodium molybdate solution was treated with calcium chloride ($CaCl_2$) at ambient temperature to convert Na_2MoO_4 to $CaMoO_4$.

$$Na_2MoO_4 + CaCl_2 \rightarrow CaMoO_4 + 2NaCl$$

The precipitated $CaMoO_4$ was filtered, washed and dried. Calcium molybdate is a low value product compared to MoO_3. Therefore, in the second method recovery of molybdenum as MoO_3 was carried out. The sodium molybdate solution was acidified with concentrated HNO_3 at ambient temperature with stirring. Na_2MoO_4 was converted to H_2MoO_4 by this treatment.

$$Na_2MoO_4 + 2HNO_3 \rightarrow H_2MoO_4 + NaNO_3$$

The precipitated molybdic acid (H_2MoO_4) was filtered, washed, dried and calcined to produce molybdenum trioxide (MoO_3). Recovery of Mo as MoO_3 was 97.5%. The recovered MoO_3 was fairly pure (purity > 98%). Its sodium content was 0.03%. Other impurities included Si (0.02%); Fe (0.05%), V (0.12%); Al (0.01%) and traces of SO_4, Cl and moisture. It is comparable to the technical grade MoO_3 product commercially available in the market and it is highly suitable for use in the steel industry.

X-ray diffraction patterns of the $CaMoO_4$ and MoO_3 products recovered by this procedure contained all characteristic peaks of these materials as shown in Fig. 3b and c confirmed that they were highly pure.

The Ni/Al_2O_3 residue, after extracting sodium molybdate and sodium vanadate, was digested with caustic soda in an autoclave under pressure at 250 °C for 3 h. The Al_2O_3 was dissolved as sodium aluminate under these conditions leaving NiO as a residue.

$$NiO + Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O + NiO$$

Ni was recovered as nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] by treating the NiO residue with nitric acid. Purity of the nickel nitrate was 98%. The contaminants present in Nickel nitrate included traces of SO4, Cl, Na, Al, Fe, Si and moisture.

The above results are in agreement with the findings of some previous studies [20,22,23], and clearly indicate that the soda ash (Na_2CO_3) roasting method is very effective for selective extraction of Mo and V from spent hydroprocessing catalyst leaving the other metals (e.g., Ni) and Al_2O_3 as residue. The recovery percentages of Mo and V were however, significantly higher in the experiments conducted in the present work than that reported in some previous studies. For instance, Chen et al. [20] reported extraction of 91.3% Mo and 90% V, and Kar et al. [23] achieved 92% extraction of Mo in soda ash roasting method, whereas in the present work, greater than 99% of both Mo and V were extracted and final recoveries of V as NH_4VO_3 and Mo as MoO_3 were 96.5% and 97.5%, respectively. A major difference between the present work and previous studies in the soda ash roasting method is related to alumina recovery in the form of pure boehmite. This point is discussed in more detail in the following section.

3.2. Boehmite recovery and its transformation to γ-Al_2O_3

Boehmite [AlO(OH)] is usually prepared by precipitation from solutions of aluminium salts and sodium aluminate under hydrothermal conditions, For example, Okada et al. [24] prepared boehmite with a variety of crystallite sizes from solutions of aluminium nitrate and sodium aluminate. Lee et al. [25] obtained boehmite from aqueous solutions of aluminium chloride and sodium hydroxide. Urea had been used as a reagent for precipitating boehmite hydrothermally from aqueous solutions of different aluminium salts such as $Al(NO_3)_3$, $Al_2(SO_4)_3$ and Al_2Cl_3 [26,27]. Hydrolysis of aluminium alkoxides had been studied by some workers to prepare boehmite with high purity [28,29]. Hydrothermal transformation of aluminium trihydroxides (e.g., bayerite, gibbsite) to boehmite had been reported [30–32]. However, information on the recovery of the alumina in the form of special grades such as boehmite and γ-alumina from spent hydroprocessing catalysts is missing in the earlier studies.

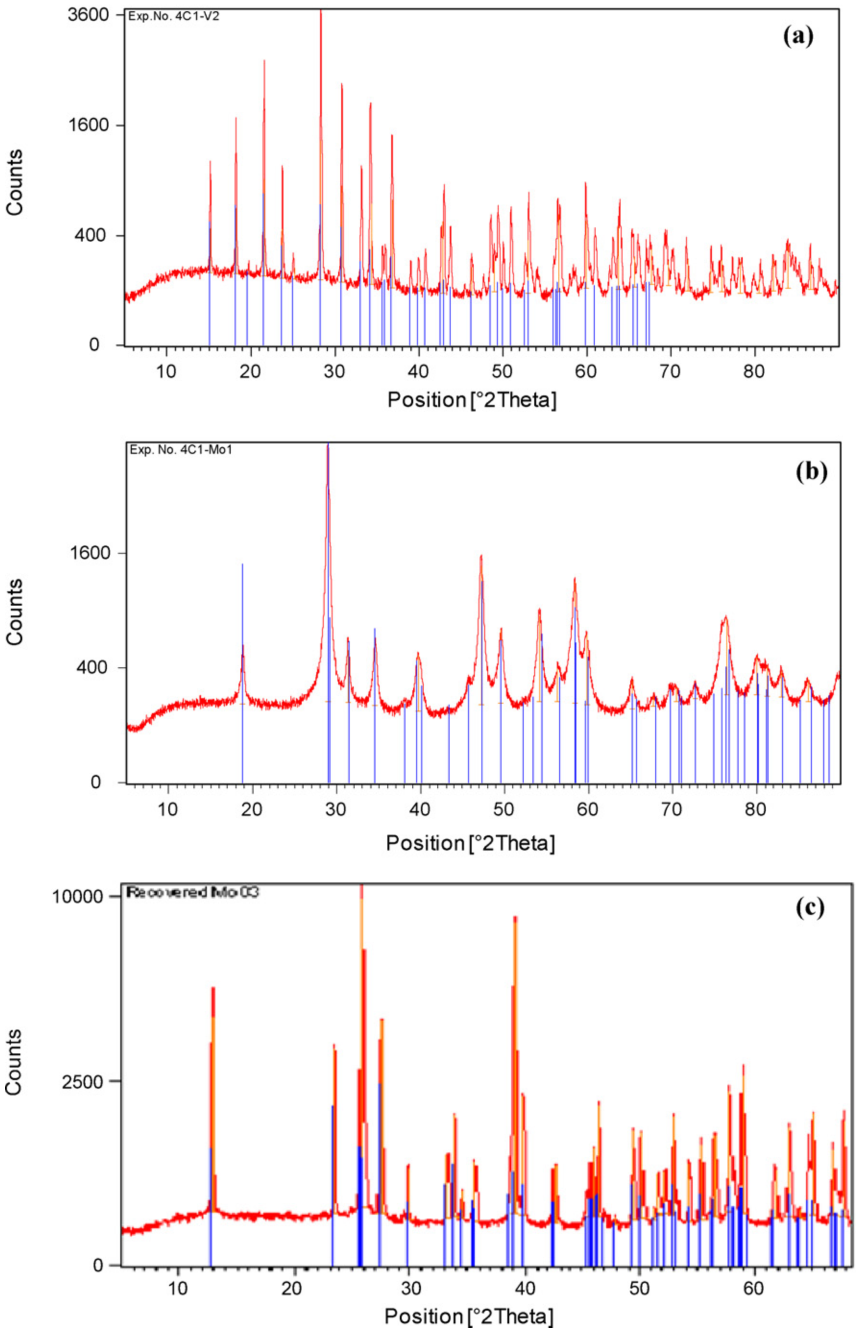


Fig. 3. XRD patterns of recovered metal salts: (a) NH_4VO_3, (b) $CaMoO_4$, and (c) MoO_3.

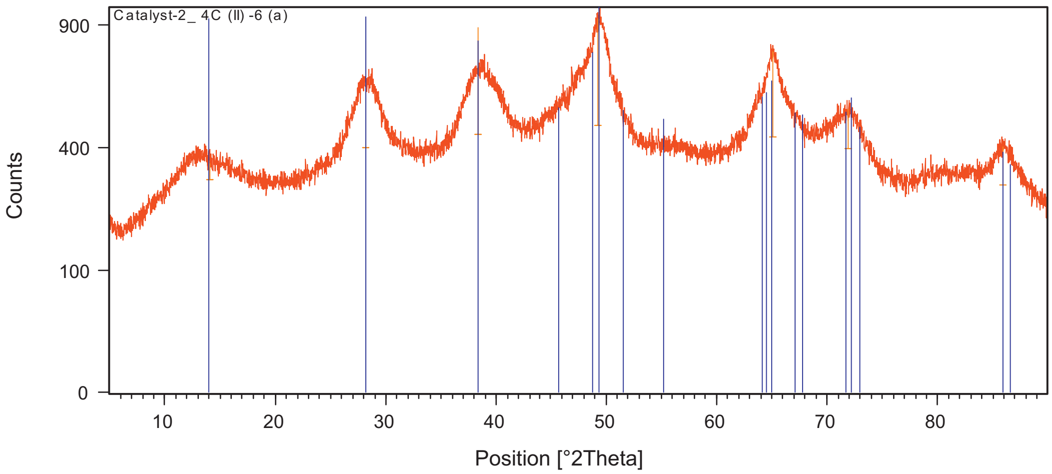
In the present study, alumina in the spent catalyst was converted to boehmite after recovering the metals. The sodium aluminate solution (pH 13) obtained by caustic digestion of the NiO/Al_2O_3 residue was treated with CO_2 to precipitate aluminium monohydroxide [AlO(OH)] gel.

$$2NaAlO_2 + CO_2(g) + H_2O \xrightarrow{\text{Precipitation}} \underset{\text{Pseudoboehmite}}{2AlO(OH)} + Na_2CO_3$$

The aluminium monohydroxide [AlO(OH)] obtained in the above reaction was found to be poorly crystallized boehmite or pseudo boehmite by XRD analysis (Fig. 4). The recovered boehmite was highly pure as indicated by XRD. Chemical analysis by ICP-AES showed that it was completely free from heavy metals (i.e. Mo, V, Ni). Its sodium content was less than 0. 02%. It was subjected to hydrothermal treatment in a high pressure autoclave in order to convert it to well crystallized boehmite and to modify its textural properties with variation in hydrothermal conditions such as temperature and time as discussed in the following section.

3.3. *Modification of the textural properties of boehmite and* γ-Al_2O_3

Since boehmite is an important precursor for γ-alumina that is used as a support for the preparation of many industrial catalysts, the recovered boehmite must have desirable textural properties (i.e., high surface area and porosity) for use in catalyst preparation. Further experiments were, therefore, continued to investigate the effect of hydrothermal treatment conditions on the crystallite and the textural properties of boehmite. The temperature and duration of hydrothermal treatment of boehmite were varied in



Ref. Code	Compound Name	Chemical Formula
00-049-0133	Pseudo boehmite	Al O (O H)

Fig. 4. XRD of recovered pseudo boehmite.

the range, 120–240 °C and 4–30 h, respectively in these experiments, and the hydrothermally treated boehmite samples were characterized by XRD analysis and by surface area and porosity measurement. Boehmite was converted to γ-Al_2O_3 by calcination at 500 °C for 4 h. Since change in boehmite properties during hydrothermal treatment can affect the properties of the γ-alumina, the textural properties of γ-alumina samples derived from different boehmite samples that were hydrothermally treated under different conditions were tested with a view to understand the relation between properties of boehmite and γ-Al_2O_3.

3.4. *Effect of hydrothermal treatment time*

The changes brought out by increasing hydrothermal treatment time in the surface area, pore volume and average pore size of boehmite and γ-alumina samples are presented in Table 1.

The surface area of boehmite increases from 194 m^2/g to 207 m^2/g when the duration of hydrothermal treatment is increased from 8 to 20 h, and then decreases drastically to 105 m^2/g with further increase of time to 40 h. The pore volume increases gradually and reaches a maximum value of 0.65 ml/g with the increase of hydrothermal treatment time from 8 to 20 h, and then decreases sharply with further increase of time to 40 h. Similar changes are observed in the surface area and pore volume values of γ-Al_2O_3 with the increase of hydrothermal treatment duration.

3.5. *Effect of hydrothermal treatment temperature*

The surface area, pore volume and average pore diameter of boehmite samples hydrothermally treated at different temperatures are compared with that of γ-Al_2O_3 samples derived from corresponding boehmite in Table 2. It can be seen that changes in boehmite properties has a strong influence on the properties of the γ-alumina. For example, with increasing hydrothermal treatment temperature, the surface area of boehmite decreases and the average pore diameter increases. A similar trend is observed in the surface area and pore diameter of γ-alumina. The changes in pore volume values of boehmite and γ-alumina with increasing temperature also show similar trends. These results clearly indicate that the textural properties of γ-alumina are closely related to that of boehmite, and any changes in boehmite properties would affect the γ-alumina properties.

The pore size distribution data for the γ-alumina samples derived from the boehmite samples hydrothermally treated at different temperatures are summarized in Table 3 and plotted in Fig. 5. Bimodal pore size distributions with narrow and large pores are observed for all samples. The γ-alumina samples prepared from the boehmite samples that were hydrothermally treated at higher temperatures have larger pores than those prepared from low temperature hydrothermally treated samples.

For example, the γ-alumina derived from the boehmite sample that was hydrothermally treated at low temperatures in the range 100–120 °C has a large percentage (42–48%) of micropores having a diameter less than 50 Å, whereas, such micropores are relatively low (8–12%) in the γ-alumina prepared from the boehmite

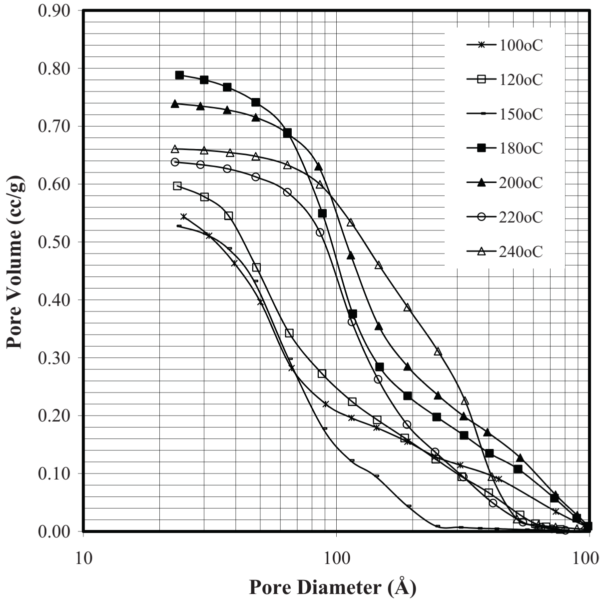


Fig. 5. Pore size distribution of γ-alumina derived from boehmite hydrothermally treated at different temperatures.

Table 1
Effect of hydrothermal treatment time on the textural properties of boehmite and γ-Al_2O_3.

Time (h)	Boehmite			γ-Al_2O_3		
	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
8	194.1	0.44	81.1	204.6	0.53	90.5
18	206.8	0.63	109.8	229.7	0.73	111.4
20	184.4	0.65	117.3	201.9	0.74	126.2
30	105.4	0.51	110.1	164.9	0.69	147.4

Table 2
Effect of hydrothermal treatment temperature on the textural properties of boehmite and γ-Al_2O_3.

Temp. (°C)	Boehmite			γ-Al_2O_3		
	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
120	226.4	0.41	58.3	276.3	0.59	72.8
150	262.9	0.46	65.4	268.7	0.61	75.5
180	244.0	0.68	96.6	269.2	0.78	101.3
200	194.4	0.65	117.3	225.1	0.74	126.2
240	117.0	0.52	173.2	149.7	0.66	170.6

samples that were subjected to hydrothermal treatment at higher temperatures in the range 180–220 °C. Pores became wider in the high-temperature treated samples. About 50% of the total pore volume in these samples is contributed by 50–100 Å diameter mesopores and another 35–40% of the pore volume is present in larger mesopores having diameter in the 100–500 Å range. Increasing hydrothermal treatment temperature to 240 °C, leads to a further widening of the pores in γ-alumina. More than 30% of the pore volume is present in 250–500 Å pores in these samples.

The above results clearly indicate that the surface area, pore size distribution of γ-alumina can be modified and controlled by controlling the hydrothermal treatment conditions (e.g. time, temperature) of boehmite precursor. γ-Alumina with desirable textural properties (i.e. surface area > 200 m^2/g; pore volume > 0.7 ml/g; mean pore diameter 100–120 Å) for use as support for hydrotreating catalysts could be obtained by optimizing boehmite hydrothermal treatment temperature and time (temperature = 180–200 °C; time = 18–20 h). These results can be explained as follows.

During hydrothermal treatment, the size of boehmite crystallites increases [33,34]. Boehmite crystallite size growth strongly depends on hydrothermal treatment temperature and time. Higher temperature and longer duration of hydrothermal treatment enhance the growth of boehmite particles leading to the formation of larger crystallites. This was confirmed by the XRD results of the hydrothermally treated boehmite samples (Fig. 6). It can be seen that the XRD peaks of boehmite samples increase in intensity and become sharper with increasing hydrothermal treatment temperature. This indicates that crystal size of the boehmite increases with increasing hydrothermal treatment temperature. The poorly crystallized pseudoboehmite is transformed to well-crystallized boehmite by hydrothermal treatment at high temperatures. Detailed calculation of boehmite crystallite size with increasing hydrothermal treatment temperature and its correlation with pore size distribution will be considered in our future studies.

The formation of larger crystallites by sintering and agglomeration of smaller particles under hydrothermal conditions will reduce the surface area. Porosity originates from the space between the particles [35]. When large crystallites get packed, the space between the particles (i.e., pore width) would be large. Pore size increase in the boehmite samples with increasing severity of hydrothermal treatment could therefore, result from the increase in boehmite crystallite size.

Increase in the pore size of γ-alumina prepared from the boehmite samples that were treated at higher temperatures and longer durations could also be explained by a similar mechanism. Boehmite is converted to γ-alumina by calcination at temperatures in the range of 450–500 °C. During calcination, dehydration of boehmite occurs with the loss of 1 mole of H_2O and forms γ-alumina. When boehmite is calcined, its hydroxide layers are destroyed, but the oxygen layers remain unaffected. There is an orientation relationship of the lattice axes between boehmite and its transition derivatives. The morphologies and other properties of the produced γ-Al_2O_3 will therefore, be similar to that of boehmite. Thus, when boehmite with large crystallites is converted to γ-alumina by calcination, the particles of γ-alumina will also be larger. As a result, the pore size of the γ-alumina will also be larger.

Alumina is the main component of spent hydroprocessing catalysts, accounting for more than 55–65 wt% depending on the amount of contaminants. Alumina is a valuable material, and it has many uses. In the present study, alumina recovery as high purity boehmite has been achieved together with the reclamation of all

Table 3
Pore size distribution data for γ-alumina samples derived from boehmite samples hydrothermally treated at different temperature.

Pore diameter (Å)	Pore volume													
	100[a]		120[a]		150[a]		180[a]		200[a]		220[a]		240[a]	
	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%
<50	0.262	48.1	0.254	42.6	0.229	43.4	0.100	12.6	0.050	7.0	0.050	8.2	0.030	4.2
50–100	0.103	18.9	0.150	25.1	0.202	38.4	0.410	51.4	0.330	45.0	0.320	50.7	0.250	37.2
100–250	0.065	11.9	0.098	16.5	0.089	16.9	0.120	15.0	0.160	21.1	0.170	26.4	0.160	24.4
250–500	0.080	14.7	0.081	13.6	0.004	0.7	0.110	13.7	0.140	18.4	0.090	13.6	0.210	32.5
500–1000	0.028	5.2	0.014	2.3	0.003	0.6	0.050	6.9	0.060	8.2	0.010	1.2	0.010	1.4
>1000	0.006	1.1	0.000	0.0	0.000	0.0	0.003	0.4	0.003	0.4	0.000	0.0	0.002	0.3
Total pore volume (cm^3/g)	0.054	100.0	0.600	100.0	0.530	100.0	0.790	100.0	0.740	100.0	0.640	100.0	0.660	100.0

[a] Temp. (°C).

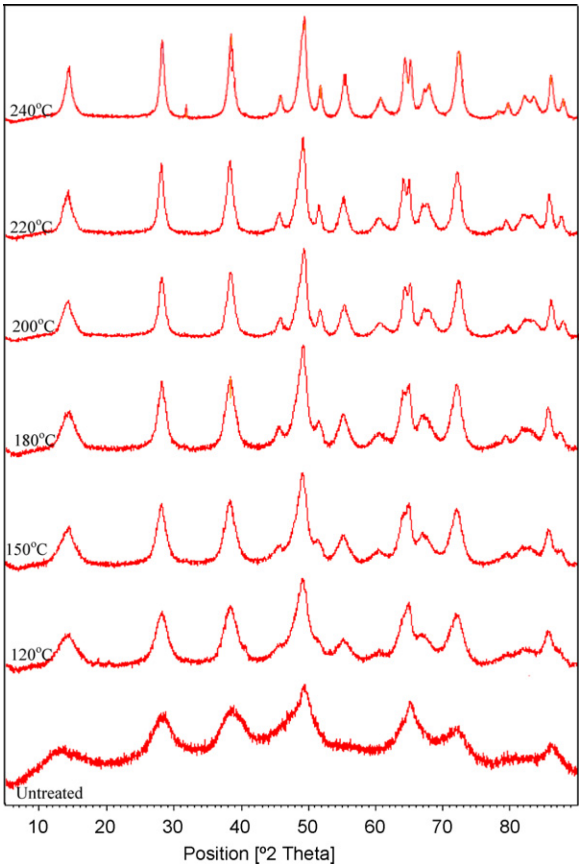


Fig. 6. X-ray diffraction patterns of recovered boehmite illustrating the effect of hydrothermal reaction temperature.

valuable metals (Mo, V, Ni) from spent hydroprocessing catalyst. Boehmite is a valuable material, and it has a wide range of applications including catalyst supports, coatings, polymer additives, sol–gel abrasives, and ceramics.

The recovered metals can be used in the steel industry for making stainless steel and special alloys. In addition, the metals have many other uses. Thus, for example, nickel is used in electroplating, coins, catalysts, and in rechargeable Ni–Cd batteries. Mo and Co compounds are used in the preparation of catalysts for petroleum refining and chemicals manufacturing. Vanadium compounds (e.g. V_2O_5) are used in the production of glass and ceramics and as an oxidizing catalyst for chemicals manufacture. Recovery of the metals and the alumina base from the spent catalysts can provide a complete solution to their environmental problem in a cost effective way.

4. Conclusion

A method for the recovery of special grades of alumina such as boehmite and γ-Al_2O_3 together with reclamation of metals (V, Mo and Ni) as metal salts from spent hydroprocessing catalyst was developed in the present study. Textural properties of the recovered boehmite and γ-Al_2O_3 were modified by hydrothermal treatment. Both boehmite and γ-Al_2O_3 with desirable textural properties (i.e. surface area > 200 m^2/g; pore volume > 0.7 ml/g; mean pore diameter 100–120 Å) suitable for use as catalyst support were obtained by optimizing boehmite hydrothermal treatment conditions.

The recovery of boehmite for reuse from spent hydroprocessing catalyst wastes together with the extraction of valuable metals not only can add more economic value to the metal recovery process, but also can lead to total recycling of such hazardous spent catalysts without leaving the residual alumina for disposal.

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